Probability distributions of the work in the 2D-Ising model

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February 6, 2008

Abstract

Probability distributions of the magnetic work are computed for the 2D Ising model by means of Monte Carlo simulations. The system is first prepared at equilibrium for three temperatures below, at and above the critical point. A magnetic field is then applied and grown linearly at different rates. Probability distributions of the work are stored and free energy differences computed using the Jarzynski equality. Consistency is checked and the dynamics of the system is analyzed. Free energies and dissipated works are reproduced with simple models. The critical exponent δ is estimated in an usual manner.

1 Introduction

The Jarzynski equality [1, 2] is one of the few exact results in the context of out-of-equilibrium statistical physics. This simple and elegant relation applies to systems initially prepared at thermal equilibrium and then driven out-of-equilibrium by varying a control parameter h from say h_1 to h_2. The probability distribution of the work W extracted during the experiment is related to the free-energy difference $\Delta F = F(h_2) - F(h_1)$ between the two equilibrium states at values h_1 and h_2 of the control parameter by:

$$e^{-\beta\Delta F} = \langle e^{-\beta W}\rangle. \tag{1}$$

Remarkably, this relation gives some information about the equilibrium state at the value h_2 of the control parameter even though this state has never been reached by the system. For a cyclic transformation, one recovers the Bochkov-Kuzovlev relation $\langle e^{-\beta W}\rangle_{\mathrm{Cycl.}} = 1$ [3]. As recognized by Crooks, the Jarzynski equality can be derived from a more general fluctuation theorem [4]. It has passed experimental, see for instance [5, 6, 7] as well as numerical [8] tests. In both cases, the importance of a sufficiently accurate sampling of the tail of the probability distribution $\wp(W)$ has been emphasized. Since the pioneering experiment on DNA by Liphardt *et al.* [5], the Jarzynski relation is now widely used in chemistry and biophysics to estimate equilibrium free energy differences based on experiments or short-time out-of-equilibrium numerical calculations. However, the way the interaction with the thermal bath is taken into account in the original Jarzynski's demonstration has been criticized [9]: the interaction is assumed to be weak enough to be neglected. It

means that the system cannot exchange heat with the bath. Equation (1) was thus claimed to fail since one expects that the system tends to relax to an equilibrium state by exchanging heat with the bath. For Jarzynski's response, see [10]. As far as we know, no experiment has provided any evidence of this failure yet. In this paper, we present a Monte Carlo study of the 2D Ising model with a Glauber dynamics. For such Markovian dynamics, the interaction with the bath is properly taken into account by the transition rates. The criticisms do not apply to this case and the demonstration given by Jarzynski in appendix of reference [2] is exact.

In the context of spin models, up to now few studies have taken advantage of the Jarzynski equality to calculate the free energy. Results have recently been obtained for a single Ising spin [11] and in the mean-field approximation [12]. We present a Monte Carlo investigation of the two-dimensional Ising model. Numerical details of the calculation are presented in the first section. The three next sections correspond to calculations with an initial equilibrium state at different temperatures: in the paramagnetic phase ($\beta = 0.2$), the ferromagnetic phase ($\beta = 0.7$) and at the critical point ($\beta \simeq 0.4407$).

2 Numerical procedure

We study the two-dimensional Ising model defined by the usual Hamiltonian

$$\mathcal{H}(\{\sigma\}) = -J\sum_{(i,j)}\sigma_i\sigma_j - h\sum_i \sigma_i, \quad \sigma_i = \pm 1 \tag{2}$$

where the sum extends over nearest-neighbors on a square lattice. In the following, the exchange coupling is fixed to $J = 1$. Lattices with sizes from 32×32 to 128×128 and periodic boundary conditions have been considered. The system is first prepared in an equilibrium state without magnetic field using the Swendsen-Wang cluster-algorithm [13]. In the paramagnetic and ferromagnetic phases, the system was first equilibrated using 200 Monte Carlo Steps (MCS). At the critical point, we used 1000 MCS to circumvent the critical slowing-down. This last value is a safe bet since it is more than two orders of magnitude larger than the autocorrelation time $\tau_E \simeq 5.87(1)$ at T_c and for $L = 128$ [14]. We then let the system evolve according to a local dynamics, i.e. using the Metropolis algorithm [15], during $n_{\text{iter.}}$ Monte Carlo iterations while the magnetic field h is linearly increased. In the following, h denotes the final magnetic field reached after $n_{\text{iter.}}$ iterations. The work is calculated as

$$W = -\int_0^h M dh = -\int_0^{t_f} M(t)\dot{h}dt \simeq -\frac{h}{n_{\text{iter.}}}\sum_{i=0}^{n_{\text{iter.}}-1} M_i \tag{3}$$

i.e. as the average magnetization during these $n_{\text{iter.}}$ iterations times the magnetic field h. Note that W is the mechanical work and not the work as usually defined in thermodynamics [16]. Let us emphasize that the demonstration of (1) given by Jarzynski at the end of his second paper on the subject [2] requires a well-defined protocol: first a sudden change Δh of the magnetic field is performed leading to a work $-\Delta h M_i$ where M_i is the magnetization and second a Monte Carlo iteration is made which allows the system to relax and exchange heat $Q = \Delta E = E_{i+1} - E_i$ with the bath. Note that when $n_{\text{iter.}} = 1$, the Jarzynski relation is equivalent to the thermodynamic perturbation. The experiment is repeated $n_{\text{exp.}} = 100,000$ times. Instead of restarting the whole simulation, we used the last spin configuration obtained without magnetic field and did 10 further Swendsen-Wang MCS at $T \neq T_c$ and 50 at T_c. This last value is almost ten times larger than the autocorrelation time. Autocorrelations between two successive experiments are thus smaller than

$\exp(-50/5.9) \simeq 2.10^{-4}$ and will be neglected in the following. Averages are computed as

$$\langle f(W)\rangle = \int f(W)\wp(W)dW = \frac{1}{n_{\rm exp.}}\sum_{\alpha=1}^{n_{\rm exp.}} f(W_\alpha) \tag{4}$$

where $\{W_\alpha\}_\alpha$ is the set of values obtained when repeating $n_{\rm exp.}$ times the numerical experiment. Errors are estimated as $\sqrt{[\langle f^2\rangle - \langle f\rangle^2]/n_{\rm exp.}}$ as expected from the central limit theorem for uncorrelated random variables.

2.1 Paramagnetic phase

As the temperature is increased in the paramagnetic phase, the correlation length becomes smaller and eventually gets smaller than the lattice spacing. One can thus consider the system as a set of free spins. The dynamical evolution of the probability distribution of each of them is governed by the Glauber master equation [17]. Since individual spins relax very rapidly to equilibrium, the probability distribution of the work $\wp(W)$ is expected to be Gaussian [11]. It is indeed what is observed numerically for $\beta = 0.2$, as can be seen in Figure 1. We have checked that there is no observable deviation from a Gaussian law in the tails. Calculation of the coefficient of excess $\gamma = \langle (W-\langle W\rangle)^4\rangle / \langle (W-\langle W\rangle)^2\rangle^2 - 3$ gives small values between 3.10^{-3} and 10^{-2} for the different simulations performed.

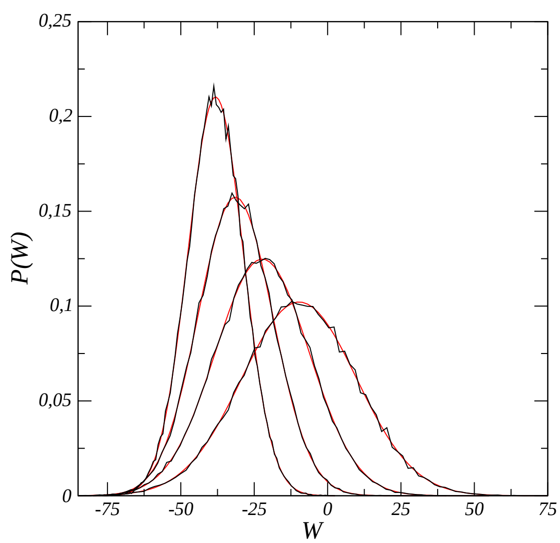

Figure 1: Probability distribution of the work in the paramagnetic phase ($\beta = 0.2$) when applying linearly a magnetic field $h = 0.1$ at different rates: $n_{\rm iter.} = 2, 5, 10$ and 20 (from right to left). The monotonous curves correspond to Gaussian fits.

The free-energy ΔF can be measured using the Jarzynski equality (1), either directly or by using the assumption that the work W is Gaussian distributed:

$$\langle e^{-\beta W}\rangle = \frac{1}{\sqrt{2\pi\sigma_W^2}}\int e^{-\beta W-(W-\langle W\rangle)^2/2\sigma_W^2}dW \Leftrightarrow \ \Delta F = \langle W\rangle - \frac{\sigma_W^2}{2k_BT}. \tag{5}$$

This last relation was first obtained by Hermans [18]. In both methods, the free energy difference should not depend on the experimental protocol, in our case the

h	$n_{\text{iter.}}$	$\langle W\rangle$	ΔF (Jarzynski)	$W_{\text{diss.}} = \langle W\rangle - \Delta F$	ΔF (Gaussian approx.)
0.1	2	$-8.83(6)$	$-4.5(1).10^1$	$3.6(1).10^1$	$-4.69(3).10^1$
0.1	5	$-2.155(5).10^1$	$-4.70(10).10^1$	$2.5(1).10^1$	$-4.70(3).10^1$
0.1	10	$-3.068(4).10^1$	$-4.8(1).10^1$	$1.7(1).10^1$	$-4.67(3).10^1$
0.1	15	$-3.523(3).10^1$	$-4.68(1).10^1$	$1.16(2).10^1$	$-4.68(3).10^1$
0.1	20	$-3.777(3).10^1$	$-4.678(9).10^1$	$9.0(1)$	$-4.68(3).10^1$
0.1	30	$-4.059(3).10^1$	$-4.683(5).10^1$	$6.23(8)$	$-4.69(2).10^1$
1.0	2	$-8.578(6).10^2$	$-1.667(5).10^3$	$3.7(1).10^3$ †	$-4.6(1).10^3$
1.0	5	$-2.0500(5).10^3$	$-2.616(2).10^3$	$2.4(2).10^3$ †	$-4.5(2).10^3$
1.0	10	$-2.9068(4).10^3$	$-3.523(5).10^3$	$1.5(2).10^3$ †	$-4.4(2).10^3$
1.0	15	$-3.3037(3).10^3$	$-3.711(5).10^3$	$1.0(2).10^3$ †	$-4.3(2).10^3$
1.0	20	$-3.5270(3).10^3$	$-3.864(4).10^3$	$0.8(2).10^3$ †	$-4.3(2).10^3$
1.0	30	$-3.7663(2).10^3$	$-4.019(3).10^3$	$0.5(2).10^3$ †	$-4.3(2).10^3$
10.	2	$-4.5445(5).10^4$	$-5.2532(5).10^4$	-	$-3.0(5).10^5$
10.	5	$-9.1721(3).10^4$	$-9.5794(5).10^4$	-	$-1.9(6).10^5$
10.	10	$-1.12169(2).10^5$	$-1.14980(5).10^5$	-	$-1.5(5).10^5$
10.	15	$-1.19695(2).10^5$	$-1.21706(4).10^5$	-	$-1.5(4).10^5$
10.	20	$-1.23634(1).10^5$	$-1.25357(5).10^5$	-	$-1.4(3).10^5$
10.	30	$-1.27737(1).10^5$	$-1.29189(5).10^5$	-	$-1.4(3).10^5$

Table 1: Estimates of the average work $\langle W\rangle$, the free energy difference ΔF, the dissipated work $\langle W\rangle - \Delta F$ and the free energy difference using the Gaussian approximation in the paramagnetic phase ($\beta = 0.2$) for different magnetic fields h and transformation rates. The estimates of the dissipated work $W_{\text{diss.}}$ marked with † have been computed using ΔF as given by the Gaussian approximation because the Jarzynski equality fails in this case to give stable values. In the case $h = 10$, we do not even give any estimate since the Gaussian approximation leads to errors bars larger than the estimate of $W_{\text{diss.}}$.

rate at which the magnetic field is grown. Our numerical results are summarized in Table 1. For a small magnetic field $h = 0.1$ (to be compared with $J = 1$), the two methods give, as expected, estimates of ΔF in agreement independently of $n_{\text{iter.}}$, i.e. of the rate at which the transformation is performed. Using the Jarzynski relation (1), the slower the transformation, i.e. the more reversible, and the more accurate the estimates are. Due to the amplification with the factor $\exp(-\beta W)$, the relevant information is in the negative tail of the distribution. Insufficient sampling of this tail may lead to deviations of the estimate of ΔF. However, these deviations remain relatively small in our system, as can be seen in Table 2. The worst case is $\Delta F = -40(2)$ obtained for $n_{\text{iter.}} = 2$ and $n_{\text{exp.}} = 1562$ while $\Delta F \simeq -46.8$ for a larger statistics. The Gaussian assumption (5) turns out to lead to estimates of ΔF less noisy than equation (1) and that do not seem to depend on $n_{\text{iter.}}$ (see Table 1). The relevant information comes in this case from the more probable part of the distribution. However, as can be seen in Table 2, the estimate gets noisier faster for low statistics than using the Jarzynski relation (1). We also checked that the free energy differences are extensive (Table 3). When intermediate magnetic fields $h = J$ are applied, the Jarzynski equality fails to give estimates of ΔF independent of the transformation rate while it is still the case for the Gaussian approximation. When larger magnetic fields are applied, the two methods fail to give estimates of ΔF for large transformation rates, i.e. $n_{\text{iter.}}$ small. A much larger statistics would be then required. As well-known in the context of thermodynamic perturbation, one can circumvent the problem by dividing the interval $[0; h]$ in smaller pieces and

resorting to several simulations to estimate ΔF in each of them.

$n_{\text{exp.}}$	$\langle W\rangle$	ΔF (Jarzynski)	$W_{\text{diss.}} = \langle W\rangle - \Delta F$	ΔF (Gaussian approx.)
1562	$-3.80(2).10^1$	$-4.67(5).10^1$	8.8(7)	$-4.7(2).10^1$
3125	$-3.76(2).10^1$	$-4.63(3).10^1$	8.7(5)	$-4.6(1).10^1$
6250	$-3.78(1).10^1$	$-4.62(2).10^1$	8.4(3)	$-4.6(1).10^1$
12,500	$-3.765(8).10^1$	$-4.63(2).10^1$	8.7(3)	$-4.65(7).10^1$
25,000	$-3.773(6).10^1$	$-4.67(2).10^1$	9.0(2)	$-4.67(5).10^1$
50,000	$-3.777(4).10^1$	$-4.68(1).10^1$	9.0(2)	$-4.68(4).10^1$
100,000	$-3.777(3).10^1$	$-4.678(9).10^1$	9.0(1)	$-4.68(3).10^1$

Table 2: Estimates of the average work $\langle W\rangle$, the free energy difference ΔF, the dissipated work $\langle W\rangle - \Delta F$ and the free energy difference using the Gaussian approximation in the paramagnetic phase $\beta = 0.2$ with $h = 0.1$ and $n_{\text{iter.}} = 20$ versus the number of experiments $n_{\text{exp.}}$ used for the calculation of the averages.

L	$n_{\text{iter.}}$	$\Delta F/L^2$ (Jarzynski)	$\Delta F/L^2$ (Gaussian approx.)
32	2	$-2.86(2).10^{-3}$	$-2.87(3).10^{-3}$
64	2	$-2.87(4).10^{-3}$	$-2.86(2).10^{-3}$
128	2	$-2.73(6).10^{-3}$	$-2.86(2).10^{-3}$
32	5	$-2.85(1).10^{-3}$	$-2.84(2).10^{-3}$
64	5	$-2.85(1).10^{-3}$	$-2.84(2).10^{-3}$
128	5	$-2.87(6).10^{-3}$	$-2.87(2).10^{-3}$
32	10	$-2.85(1).10^{-3}$	$-2.86(2).10^{-3}$
64	10	$-2.849(7).10^{-3}$	$-2.85(1).10^{-3}$
128	10	$-2.94(7).10^{-3}$	$-2.85(2).10^{-3}$
32	20	$-2.865(8).10^{-3}$	$-2.87(1).10^{-3}$
64	20	$-2.850(5).10^{-3}$	$-2.85(1).10^{-3}$
128	20	$-2.855(5).10^{-3}$	$-2.85(2).10^{-3}$

Table 3: Estimates of the free energy difference ΔF in the paramagnetic phase ($\beta = 0.2$ and $h = 0.1$) for different lattice sizes L and transformation rates $h/n_{\text{iter.}}$.

The results presented above can be understood by assuming that the system behaves as N independent Ising domains with an average magnetic moment m. The free energy difference between the equilibrium states with and without magnetic field h reads

$$\Delta F = F(h) - F(0) = -Nk_BT \ln\cosh\frac{mh}{k_BT} \tag{6}$$

The numerical data are in very good agreement with this law as can be seen in Figure 2. The best fit is obtained for the parameters $N \simeq 0.13L^2$ and $m \simeq 4.62$ which means that the characteristic size of the domains is of the order of $\xi \sim \sqrt{L^2/N} \simeq 2.8$ and that the domains are not at saturation, $Nm/L^2 \simeq 0.6$. At equilibrium, the magnetization is expected to be

$$M_{\text{eq.}}(h) = -\frac{\partial F}{\partial h} = Nm\tanh\frac{mh}{k_BT} \simeq N\frac{m^2h}{k_BT} \tag{7}$$

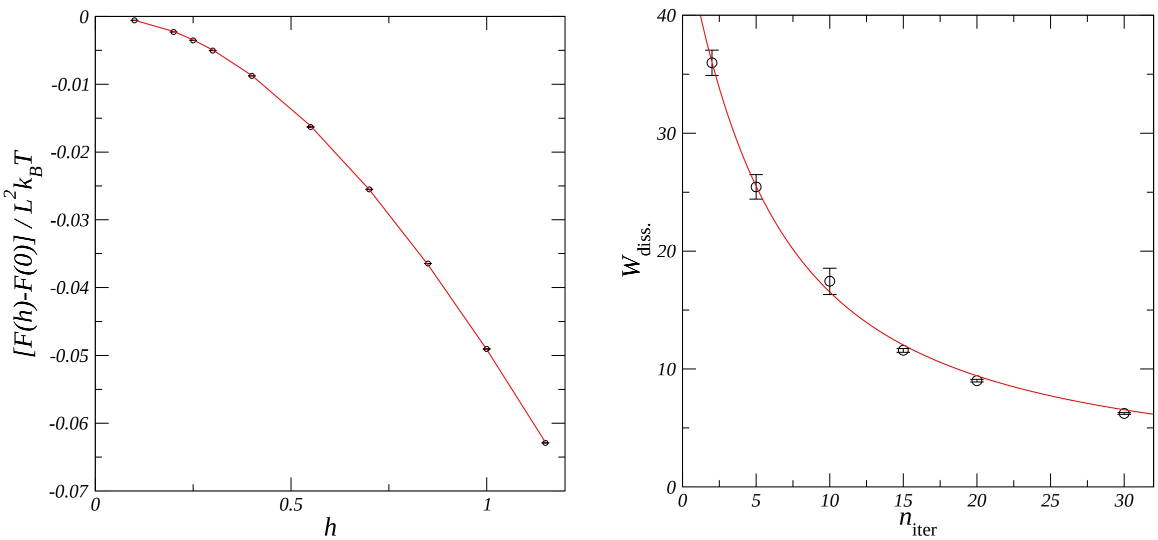

Figure 2: On the left, free energy density $\Delta F/L^2$ versus the final applied magnetic field h in the paramagnetic phase ($\beta = 0.2$) for the slowest transformation rate considered ($n_{\rm iter.} = 30$). The curve corresponds to a non-linear fit with the expression (6). On the right, dissipated work $W_{\rm diss.}$ with respect to the number of Monte Carlo iterations $n_{\rm iter.}$ for $h = 0.1$. The curve is a two-parameter non-linear fit with the expression (11).

Let us assume the phenomenological evolution equation

$$\frac{\partial M}{\partial t} = -\frac{M(t) - M_{\rm eq.}(h)}{\tau} \ \Leftrightarrow\ M(t) = M(0)e^{-t/\tau} + \frac{1}{\tau}\int_0^t M_{\rm eq.}(h(t'))e^{-(t-t')/\tau}dt' \tag{8}$$

where τ is the relaxation time. The work extracted from the system when the magnetic field is increased linearly, i.e. $h(t) = \dot{h}t$, reads

$$\begin{aligned} W = -\dot{h}\int M(t')dt' &= -\dot{h}M(0)\big(1 - e^{-t/\tau}\big) - \frac{\dot{h}}{\tau}\int_0^t\int_0^{t'} M_{\rm eq.}(h(t''))e^{-(t'-t'')/\tau}dt'dt'' \\ &\simeq -\dot{h}M(0)\big(1 - e^{-t/\tau}\big) - \frac{\dot{h}^2 Nm^2}{\tau k_B T}\int_0^t\int_0^{t'} t'' e^{-(t'-t'')/\tau}dt'dt'' \\ &= -\dot{h}M(0)\big(1 - e^{-t/\tau}\big) - \frac{\dot{h}^2 Nm^2}{k_B T}\left[\frac{1}{2}t^2 - \tau t + \tau^2\left(1 - e^{-t/\tau}\right)\right] \end{aligned} \tag{9}$$

where $M_{\rm eq.}$ has been replaced by its weak-field expansion (7). Starting the experiment from the paramagnetic phase, i.e. $M(0) = 0$, and subtracting the reversible work

$$W_{\rm rev.} = -\dot{h}\int M_{\rm eq.}(t')dt' \simeq -\frac{\dot{h}^2 Nm^2}{2k_B T}t^2 \tag{10}$$

one gets finally

$$W_{\rm diss.} \simeq \frac{\dot{h}^2 Nm^2}{k_B T}\left[\tau t - \tau^2\left(1 - e^{-t/\tau}\right)\right] = \dot{h}M_{\rm eq.}(h)\tau\left[1 - \frac{\tau}{t}\left(1 - e^{-t/\tau}\right)\right] \tag{11}$$

As can be seen in Figure 2, the expression fits well the numerical data for $h = 0.1$. The non-linear fit gives $\tau \simeq 2.23$ for the relaxation time and $m \simeq 4.72$ assuming $N = 0.13L^2$. Note that the estimate m is compatible with the one calculated from

ΔF ($m \simeq 4.62$). The estimate of the relaxation time τ is small as expected for such a high temperature. For larger magnetic fields, the dissipated work is still nicely fitted by the expression (11) but the fit gives too small average moments m. This is due to the fact that the expression (11) was derived in the weak magnetic field limit.

2.2 Ferromagnetic phase

In the ferromagnetic phase $\beta = 0.7$, the probability distributions $\wp(W)$ display two well-separated peaks corresponding to the work performed by systems in each one of the two initial ferromagnetic ground states. The average $\langle e^{-\beta W}\rangle$ is dominated by the peak at more negative values of the work. As a consequence, the Gaussian approximation applied only to this peak leads to estimates of ΔF in very good agreement with those obtained with the Jarzynski equality (Table 4). Since the two peaks are not centered around zero, averages over the most negative peak were computed in practise by selecting configurations for which the work W is smaller than the average of the smallest and largest works. A large gap separating the two peaks, the average work would have given the same results. As can be seen in Table 4, the estimates of ΔF do not show any dependence on the transformation rate and give compatible values using the Jarzynski equation (1) and the Gaussian approximation (5).

h	$n_{\text{iter.}}$	$\langle W\rangle$	ΔF (Jarzynski)	$W_{\text{diss.}} = \langle W\rangle - \Delta F$	ΔF (Gaussian approx.)
0.1	10	$1.0(5).10^1$	$-1.622740(7).10^3$	$1.633(5).10^3$	$-1.624(5).10^3$
0.1	50	$7(5)$	$-1.622732(5).10^3$	$1.629(5).10^3$	$-1.624(2).10^3$
0.1	250	$4(5)$	$-1.622735(5).10^3$	$1.627(5).10^3$	$-1.624(1).10^3$
1.0	10	$-2.4(5).10^2$	$-1.63057(3).10^4$	$1.607(5).10^4$	$-1.63(4).10^4$
1.0	50	$-1.40(5).10^3$	$-1.630612(4).10^4$	$1.490(5).10^4$	$-1.63(2).10^4$
1.0	250	$-6.22(3).10^3$	$-1.6306156(9).10^4$	$1.009(3).10^4$	$-1.631(7).10^4$
10.	10	$-1.076(2).10^5$	$-1.63676(1).10^5$	$5.61(2).10^4$	$-1.6(2).10^5$
10.	50	$-1.3313(10).10^5$	$-1.637355(8).10^5$	$3.061(10).10^4$	$-1.64(7).10^5$
10.	250	$-1.4475(6).10^5$	$-1.637402(2).10^5$	$1.899(6).10^4$	$-1.64(3).10^5$

Table 4: Estimates of the average work $\langle W\rangle$, the free energy difference ΔF, the dissipated work $\langle W\rangle - \Delta F$ and the free energy difference using the Gaussian approximation with the most negative peak in the ferromagnetic phase ($\beta = 0.7$) for different magnetic fields h and transformation rates $h/n_{\text{iter.}}$.

In a sense, the physics is simpler than in the paramagnetic phase. Before applying the magnetic field, the initial magnetization is either $+M_0$ or $-M_0$ with small fluctuations around these two values. When applying a small magnetic field, i.e. $h = 0.1$ in our case, the magnetization does not change much so that the work is either $-M_0h$ or $+M_0h$. According to Jarzynski equation (1), the free energy reads

$$\Delta F = -k_BT\ln\langle e^{-\beta W}\rangle = -k_BT\ln\left[\frac{1}{2}e^{-\beta M_0 h} + \frac{1}{2}e^{\beta M_0 h}\right] \simeq -M_0h + k_BT\ln 2 \quad (12)$$

Using the saturation magnetization $M_{\text{sat}} = L^2 = 16384$, one obtains indeed a good estimate of ΔF. The average work is small $\langle W\rangle = (-M_0h + M_0h)/2 = 0$ so that the dissipated work is $W_{\text{diss.}} = \langle W\rangle - \Delta F \simeq -\Delta F$. For larger magnetic fields, $h = 1$ and $h = 10$, this approximation is not valid anymore: the magnetization tends to reverse itself if it was initially in the opposite direction of the field. However, since the

Jarzynski equality (1) is dominated by the systems for which the magnetization was initially in the same direction than the field, one still expects that $\Delta F \simeq -M_{\text{sat}} h$. But the average magnetization now moves towards $-M_{\text{sat}}$ so $W_{\text{diss.}} > 0$. Obviously dissipation is thus mainly due to the systems for which the initial magnetization was in the "wrong" direction.

2.3 Critical point

We now present results at the critical point $\beta_c = \frac{1}{2}\ln\left(1+\sqrt{2}\right) \simeq 0.440687$. Like in the ferromagnetic phase, the probability distributions $\wp(W)$ display two well-separated peaks. Due to finite-size effects, the initial state has indeed a non-vanishing magnetization of sign either positive or negative due to the Z_2 symmetry ($\sigma_i \to -\sigma_i$) of the Ising model. In contradistinction to the ferromagnetic case, the two peaks do not have a Gaussian shape. The free energy differences ΔF calculated from the Jarzynski equation (1) are presented for two different magnetic fields in Table 5. For the smallest magnetic field $h \simeq 0.023$, the free-energy turns out to be independent of the transformation rate $h/n_{\text{iter.}}$: the maximum deviation from the average is of the order of one standard deviation. For the largest magnetic field $h \simeq 0.23$, a systematic deviation is observed.

h	$n_{\text{iter.}}$	$\langle W\rangle$	ΔF (Jarzynski)	$W_{\text{diss.}} = \langle W\rangle - \Delta F$
0.022692	2	$-1.6(7)$	$-2.690(7).10^2$	$2.67(1).10^2$
0.022692	10	$-1.1(7)$	$-2.697(4).10^2$	$2.69(1).10^2$
0.022692	50	$-7.5(7)$	$-2.704(5).10^2$	$2.63(1).10^2$
0.022692	100	$-1.39(7).10^1$	$-2.701(4).10^2$	$2.56(1).10^2$
0.022692	150	$-1.85(7).10^1$	$-2.698(2).10^2$	$2.513(8).10^2$
0.022692	250	$-2.87(7).10^1$	$-2.699(1).10^2$	$2.411(8).10^2$
0.226918	2	$-2.4(7).10^1$	$-2.897(2).10^3$	$2.873(9).10^3$
0.226918	10	$-1.87(7).10^2$	$-3.009(2).10^3$	$2.822(9).10^3$
0.226918	50	$-7.93(6).10^2$	$-3.103(1).10^3$	$2.310(7).10^3$
0.226918	100	$-1.362(5).10^3$	$-3.133(2).10^3$	$1.771(6).10^3$
0.226918	150	$-1.680(4).10^3$	$-3.136(2).10^3$	$1.456(6).10^3$
0.226918	250	$-2.017(3).10^3$	$-3.143(1).10^3$	$1.126(4).10^3$

Table 5: Estimates of the average work $\langle W\rangle$, the free energy difference ΔF, the dissipated work $\langle W\rangle - \Delta F$ at the critical point for two different transformation rates $h/n_{\text{iter.}}$ and two magnetic fields h.

We made simulations for ten values of the final magnetic field in the range $h \in [0.023; 0.23]$. The singular part of the free-energy is expected to scale at the critical point as

$$F_{\text{sing.}}(h) \underset{T\to T_c, h\ll 1}{\sim} h^{1+1/\delta} \tag{13}$$

Neglecting the contribution of the regular part, we fitted ΔF as given by the Jarzynski equality with the scaling form (13). The data display a nice power-law behavior but fluctuations are observed for fast transformations ($n_{\text{iter.}} \leq 10$) at large magnetic fields. The estimates of $1+1/\delta$ and δ are collected in Table 6. As the transformation gets slower, and thus $n_{\text{iter.}}$ larger, the numerical estimate gets closer to the exact result $\delta = 15$. For the fastest transformation $n_{\text{iter.}} = 2$, the relative deviation of the numerical estimate from the exact result is of order of 100%! Note however that much better estimates are obtained when restricting the fit to the smallest values of the magnetic field: $\delta = 19.9(7)$ for $h \leq 0.018$ and $\delta = 14.1(6)$ for $h \leq 0.013$ when $n_{\text{iter.}} = 2$. Since error bars take into account all sources of statistical fluctuations,

the deviation may be explained as a systematic bias due to a too small number of experiments for the calculation of the average. As can be seen in Table 7, when $n_{\text{exp.}}$ is made smaller the estimate of δ indeed increases. The effect is dramatic for fast transformations: a relatively good estimate of δ is already obtained for $n_{\text{iter.}} = 250$ when averaging over only $n_{\text{exp.}} = 1000$ experiments but the same deviation from the exact result $\delta = 15$ is not even obtained with $n_{\text{exp.}} = 100,000$ experiments for $n_{\text{iter.}} = 50$. More stable estimates of δ are obtained for a smaller system, $L = 64$, for which δ does not display a systematic deviation but fluctuates between 14.0(1) ($n_{iter} = 2$) and 14.1(2) ($n_{iter} = 150$) and remains below the exact value because of finite-size effects.

$n_{\text{iter.}}$	$1 + 1/\delta$	δ
2	1.024(7)	42(1)
10	1.045(6)	22.2(3)
50	1.059(5)	17.0(1)
100	1.064(4)	15.7(1)
150	1.065(3)	15.36(7)
250	1.066(2)	15.13(5)

Table 6: Critical exponents $1 + 1/\delta$ and δ obtained by power-law interpolation of the free energy $\Delta F = F(h) - F(0) \sim h^{1+1/\delta}$ with ten magnetic fields in the range $[0.023; 0.23]$ at the critical point for different transformation rates $h/n_{\text{iter.}}$.

$n_{\text{exp.}}$	$1 + 1/\delta$	δ
10^2	1.060(10)	16.6(3)
10^3	1.066(7)	15.1(2)
10^4	1.065(3)	15.44(8)
10^5	1.066(2)	15.13(5)

Table 7: Critical exponents $1 + 1/\delta$ and δ obtained by power-law interpolation of the free energy $\Delta F = F(h) - F(0) \sim h^{1+1/\delta}$ with ten magnetic fields in the range $[0.023; 0.23]$ at the critical point for different number of experiments $n_{\text{exp.}}$ in the slowest case $n_{\text{iter.}} = 250$.

As already mentioned, the two-peak structure of the probability distribution of the work $\wp(W)$ differs from the ferromagnetic case. As can be seen in Figure 3, the left peak, which dominates the average in the Jarzynski equality (1) and thus the free energy difference ΔF, moves monotonously to the left as the magnetic field is increased. The right peak moves first to the right, up to a certain magnetic field before pursing to the left. This behavior can be understood by assuming that the dynamics of the magnetization is governed by the Langevin equation

$$\frac{\partial M}{\partial t} = -\frac{\delta \mathcal{F}}{\delta M} \simeq \kappa h(t) \;\Leftrightarrow\; M(t) \simeq M(0) + \kappa \int_0^t h(t')dt' \tag{14}$$

where the link with equation (8) is made by considering κ as a magnetic susceptibility divided by the relaxation time τ. It is sufficient for the discussion to consider κ as constant. For a single realization, the initial magnetization $M(0)$ is non-zero due to finite-size effects. When the field is increased linearly, i.e. $h(t) = \dot{h}t$, the

work extracted from the system up to time t is

$$W = -\int_0^t M(t)\dot{h}dt = -M(0)\dot{h}t - \frac{\kappa}{6}\dot{h}^2t^3 = -M(0)h - \frac{\kappa}{6}h^2t \tag{15}$$

When $M(0) < 0$, the work initially increases and eventually at $h_t = 3|M(0)|/\kappa t$ starts to decrease as can be observed in Figures 3 and 4. In our case, no turning point is observed for $n_{\rm iter.} = 10$ because the magnetic fields remain too small. The data presented in the inset of figure 4 reproduce the linear behavior of $\big(W/h - W_0\big)/n_{\rm iter.}$ versus h predicted by equation (15). Higher order terms are observed only for the slowest transformations. When the initial magnetization is initially in the same direction as the magnetic field, i.e. $M(0) > 0$, the work is always negative. For very slow transformation rate, the magnetization is expected to follow the magnetic field, i.e. to behave as the equilibrium magnetization $M_{\rm eq.} \sim h^{1/\delta}$. Taking into account the magnetic field dependence of the κ, one should expect in this case the solution of the Langevin equation (14) to scale as

$$W_{\rm rev.} \sim -\int_0^h {h'}^{1/\delta} dh' \sim -h^{1+\frac{1}{\delta}} \tag{16}$$

This behavior is indeed observed: a power-law interpolation of the position of the left peak versus the magnetic field leads to exponents $\delta = 14(1)$ for $n_{\rm iter} = 150$ and 250 compatible with the exact result $\delta = 15$.

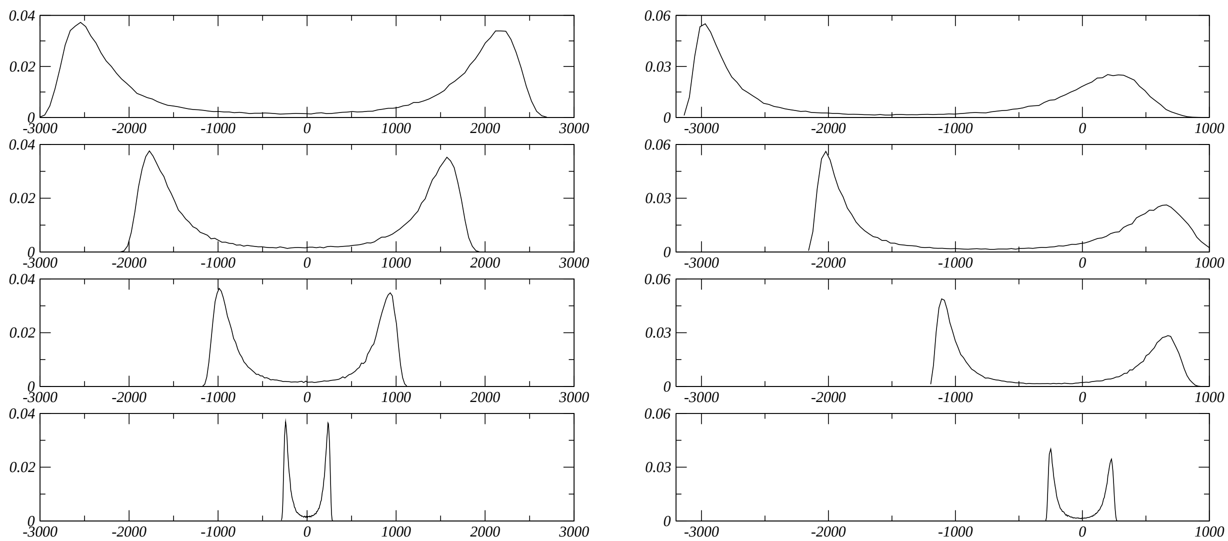

Figure 3: On the left, probability distributions $\wp(W)$ versus the work W for a fast transformation $n_{\rm iter.} = 10$ for four different final magnetic fields $h = 0.004, 0.017, 0.031$ and 0.044 (from bottom to top). On the right, probability distribution $\wp(W)$ versus W for an intermediate transformation $n_{\rm iter.} = 100$ for the same values of the magnetic field (from bottom to top).

3 Conclusions

The Jarzynski equality offers the possibility to estimate free energy differences in a very simple manner in Monte Carlo simulations. Despite the fact that this relation

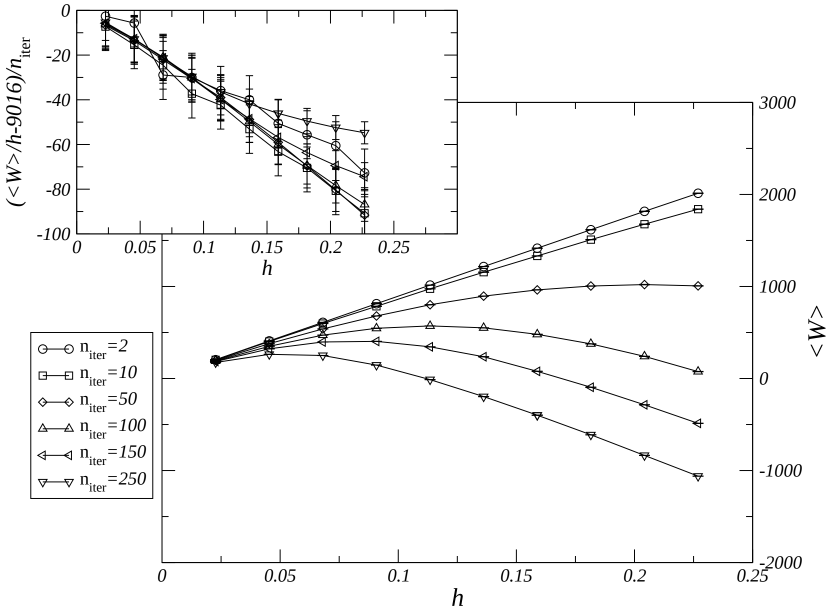

Figure 4: Average work $\langle W \rangle$ of the right peak of the probability distribution at the critical point versus the final magnetic field h for different transformation rates, i.e. $n_{\text{iter.}}$ from 2 to 250. In the inset, $\big(\langle W \rangle / h - M_0\big)/n_{iter.}$ where M_0 has been adjusted to the value $M_0 = 9016$ is plotted versus h to check the linear behavior predicted by (15).

is exact in the case of a Markovian dynamics, it has to be used carefully. As already shown by several authors, we observed systematic deviations for strongly irreversible transformations due to an insufficient sampling. These systematic deviations are caused by the fact that the average $\langle e^{-\beta W} \rangle$ is dominated by very rare events $-W \gg 1$ that may require a large number of simulations to be properly sampled. This limitation of the Jarzynski equality is a strong one: the error cannot be estimated simply. When the distribution of the work is Gaussian, it has been shown that the number of experiments has to be grown exponentially with the dissipated work $W_{\text{diss.}}$ [19]. We have observed that the Gaussian approximation (5) may still give reliable estimates of the free energy difference ΔF when the Jarzynski equality fails as for example in the case of intermediate magnetic fields applied on a paramagnet. Unfortunately, the Gaussian approximation is valid only for one-particle systems [20, 21] or systems with short-range correlations like paramagnets but not at the critical point. However, the Jarzynski equality turned out to be useful at small magnetic field. It was reliable enough for instance to estimate the critical exponent δ. For this purpose, the Jarzynski equality may be useful since a single Monte Carlo simulation is required if the work is measured at different times.

Acknowledgements

The laboratoire de Physique des Matériaux is Unité Mixte de Recherche CNRS number 7556. The authors would like to thank the Statistical Physics group and especially Olivier Collet for stimulating and illuminating discussions and Bertrand Berche for critical reading of the paper.

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